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Review

Properties relations

Entropy of Mixing, Partial Molar Quantities

热力学关系式的应用

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \quad \text{p.65, 2.13} \quad \left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$\left(\frac{\partial \Delta G}{\partial p}\right)_T = \Delta V \quad \left(\frac{\partial C_p}{\partial p}\right)_T \quad \left(\frac{\partial T}{\partial p}\right)_S \quad \left(\frac{\partial T}{\partial \sigma}\right)_S$$

$$-\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T \quad \left(\frac{\partial T}{\partial H}\right)_S \quad \left(\frac{\partial \varepsilon}{\partial H}\right)_{S,\sigma}$$



Index of nomenclature

Equilibrium: 平衡

Phase equilibrium: 相平衡

First order transitions: 一级相变

Second-order transition: 二级相变



Introduction to equilibrium

- The concept of equilibrium is fundamental
- Stable, unchanging with time and certain properties of the system are uniform throughout
- The system may not be homogeneous in form
 - Co-existence of ice and water
- Phase
 - A portion of matter that is uniform throughout, not only in chemical composition, but also in physical state
 - The usefulness of many metallic, polymeric, and ceramic systems depends on the presence, at equilibrium, of various different phases in the material



Condition of equilibrium

- Two states are in equilibrium when no reversible work can be done by having the system change between those two states

$$\delta W_{rev.1 \rightarrow 2} = 0$$

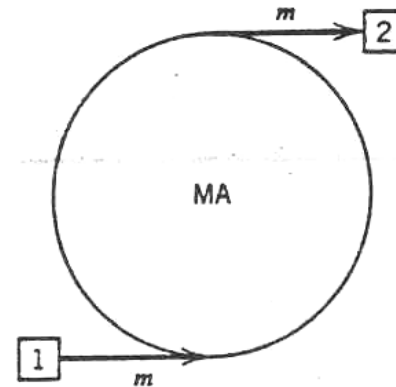


Figure 4.1 Machine MA to transform mass m from state 1 to state 2.

- The temperatures in the two states must be equal
 - A consequence of the second law of thermodynamics
 - Otherwise...



Condition of equilibrium (2)

Deal with partial molar quantities

First law

$$\left(\overline{H} + \underline{PE} + \underline{KE}\right)_{i,1} dn_{i,1} - \left(\overline{H} + \underline{PE} + \underline{KE}\right)_{i,2} dn_{i,2} + \delta Q + \delta W = dU$$

Second law

$$\overline{S}_{i,1} dn_{i,1} - \overline{S}_{i,2} dn_{i,2} + \frac{\delta Q}{T} - \frac{\delta l_w}{T} = dS$$

$$-T\overline{S}_{i,1} dn_{i,1} + T\overline{S}_{i,2} dn_{i,2} - \delta Q + \delta l_w = -TdS$$

The properties of the machine do not change at steady state

$$dU=0 \text{ and } dS=0$$

$$\left(\overline{G} + \underline{PE} + \underline{KE}\right)_{i,2} dn_{i,2} - \left(\overline{G} + \underline{PE} + \underline{KE}\right)_{i,1} dn_{i,1} = \delta W_{rev}$$



Condition of equilibrium (3)

$$\left(\overline{G} + \underline{PE} + \underline{KE}\right)_{i,2} dn_i - \left(\overline{G} + \underline{PE} + \underline{KE}\right)_{i,1} dn_i = \delta W_{rev}$$

Condition of equilibrium $\delta W_{rev.1 \rightarrow 2} = 0$

$$\left(\overline{G} + \underline{PE} + \underline{KE}\right)_{i,2} dn_i = \left(\overline{G} + \underline{PE} + \underline{KE}\right)_{i,1} dn_i$$

At the same potential energy level and kinetic level

$$\left(\overline{G}_{i,2} - \overline{G}_{i,1}\right) dn_i = \Delta \overline{G}_i = 0 \quad \overline{G}_{i,2} = \overline{G}_{i,1}$$

$$\mu_{i,2} = \mu_{i,1} \quad \text{In term of the chemical potential of } i$$

States 1 and 2 are in equilibrium with respect to material i if the partial molar Gibbs free energy (or chemical potential) of i is the same in both states.



Condition of equilibrium (4)

$$\mu_{i,2} = \mu_{i,1}$$

For single-component

$$(\underline{G}_2 - \underline{G}_1)dn = \Delta \underline{G}dn = \delta W_{rev}$$

If the difference in Gibbs free energy between the two states 1 and 2 is negative, then the reversible work term is negative. That means that the material may change spontaneously from state 1 to state 2 because no work needs to be done to force the change; in fact, work can be generated by the change. The potential to do so might be dissipated as lost work, but the potential to do reversible work exists.



Barometric equation

- The points 1 and 2 are at different altitudes. If the two are at equilibrium.

$$\underline{G}_2 - \underline{G}_1 + Mg(z_2 - z_1) = 0$$

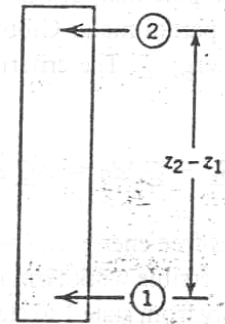


Figure 4.2 Equilibrium between top and bottom of a column of gas at constant temperature.

At constant temperature, assuring ideal gas behavior

$$d\underline{G} = \underline{V}dp = \frac{RT}{p} dp = RTd(\ln p) \quad \underline{G}_2 - \underline{G}_1 = RT \ln \frac{p_2}{p_1}$$

$$RT \ln \frac{p_2}{p_1} + Mg(z_2 - z_1) = 0$$

$$p_2 = p_1 \exp\left[-\frac{Mg}{RT}(z_2 - z_1)\right]$$

Represent the variation of pressure with height for an ideal gas.



Phase equilibrium

When a material composed of a single component exists in different physical states, the two states will be at equilibrium when the molar Gibbs free energies of the two states are equal.



Phase equilibrium (2)

For an ideal gas

$$\Delta \underline{G} = RT \ln \frac{p_2}{p_1}$$

For an incompressible solid

$$\Delta \underline{G} = \underline{V}_0 (p_2 - p_1)$$

For an compressible solid

$$\Delta \underline{G} = \frac{\underline{V}_0}{\beta_T} [1 - \exp(-\beta_T p)]$$

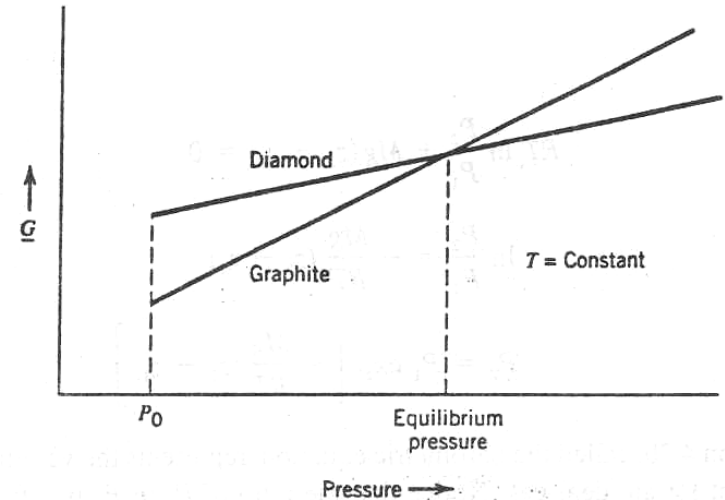


Figure 4.3 Specific Gibbs free energy versus pressure at constant temperature for graphite and diamond.

p_0 is taken as zero

Compressibility coefficient
at constant temperature



Special case: closed system, constant volume

Partial derivative of the property with respect to the mass of material i at constant temperature, volume, and the mass of other materials.

First law

$$\delta Q + \delta W = (\tilde{U}_2 - \tilde{U}_1) dn_i$$

Second law

$$(\tilde{S}_2 - \tilde{S}_1) dn_i = \frac{\delta Q}{T} - \frac{\delta l w}{T}$$

$$\delta W_{rev} = (\tilde{U}_{i,2} - \tilde{U}_{i,1}) dn_i - T(\tilde{S}_{i,2} - \tilde{S}_{i,1}) dn_i$$

$$\tilde{U} = \left(\frac{\partial U}{\partial n_i} \right)_{T, V, n_j \neq n_i}$$

$$\tilde{S} = \left(\frac{\partial S}{\partial n_i} \right)_{T, V, n_j \neq n_i}$$



Special case: closed system, constant volume (2)

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Phase Transformation and Applications

$$\delta W_{rev} = (\tilde{U}_{i,2} - \tilde{U}_{i,1})dn_i - T(\tilde{S}_{i,2} - \tilde{S}_{i,1})dn_i$$

$$\tilde{U} = \left(\frac{\partial U}{\partial n_i} \right)_{T,V,n_j \neq n_i}$$

At equilibrium

$$\tilde{F}_{i,2} = \tilde{F}_{i,1} \quad \mu_{i,2} = \mu_{i,1}$$

$$\tilde{S} = \left(\frac{\partial S}{\partial n_i} \right)_{T,V,n_j \neq n_i}$$

$$\tilde{F} = \left(\frac{\partial F}{\partial n_i} \right)_{T,V,n_j \neq n_i} = \mu_i$$

Helmholtz free energy is used to derive the chemical potential in this constant volume case.

Helmholtz and Gibbs free energy are not appreciably different in the case of solids, the work of theorists is thus made easier.



First order transitions: variation of equilibrium pressure with temperature

A one-component material exists at equilibrium in two physical states, A and B

$$\underline{G}_A = \underline{G}_B$$

Two states remain in equilibrium as temperature and pressure change, the changes in each of the molar Gibbs free energies must be the same.

$$\underline{dG}_A = \underline{dG}_B$$



First order transitions: variation of equilibrium pressure with temperature (2)

$$\underline{dG}_A = \underline{dG}_B$$

$$\left(\frac{\partial \underline{G}}{\partial T} \right)_p = -\underline{S} \quad \left(\frac{\partial \underline{G}}{\partial p} \right)_T = -\underline{V}$$

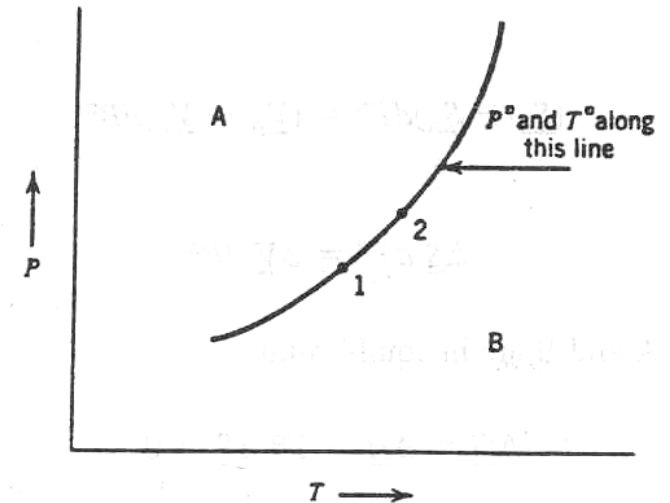


Figure 4.4 Pressure–temperature relationship for equilibrium between phases A and B.

First-order transition

The first derivatives are discontinuous at G-T

Second-order transition

The first derivative may be continuous and the second derivatives are discontinuous.



First order transitions: variation of equilibrium pressure with temperature (3)

Vapor pressure curve / phase equilibrium line

The values on this curve represent the pressure of water vapor in equilibrium with pure liquid water at the same pressure at the specified temperature

$$\underline{dG}_A = -\underline{S}_A dT^{eq} + \underline{V}_A dp^{eq}$$

$$\underline{dG}_B = -\underline{S}_B dT^{eq} + \underline{V}_B dp^{eq}$$

$$\underline{dG}_A = \underline{dG}_B = -\underline{S}_A dT^{eq} + \underline{V}_A dp^{eq} = -\underline{S}_B dT^{eq} + \underline{V}_B dp^{eq}$$

$$(\underline{S}_B - \underline{S}_A) dT^{eq} = (\underline{V}_B - \underline{V}_A) dp^{eq}$$

$$\underline{\Delta S} dT^{eq} = \underline{\Delta V} dp^{eq}$$



First order transitions: variation of equilibrium pressure with temperature (4)

$$\Delta \underline{S} dT^{eq} = \Delta \underline{V} dp^{eq}$$

$$\Delta \underline{G} = \Delta \underline{H} - T^{eq} \Delta \underline{S} = 0$$

$$\Delta \underline{S} = \frac{\Delta \underline{H}}{T^{eq}}$$

$$\Delta \underline{H} \frac{dT^{eq}}{T^{eq}} = \Delta \underline{V} dp^{eq}$$

$$\frac{dp^{eq}}{dT^{eq}} = \frac{\Delta \underline{H}}{T^{eq} \Delta \underline{V}}$$

Clapeyron equation



First order transitions: variation of equilibrium pressure with temperature (5)

$$\frac{dp^{eq}}{dT^{eq}} = \frac{\Delta H}{T^{eq} \Delta V} \quad \text{Clapeyron equation}$$

Consider the change of the melting point of tin resulting from a pressure change of 500 atm

$$\frac{\Delta p^{eq}}{\Delta T^{eq}} = \frac{\Delta H}{T^{eq} \Delta V} = \frac{7196}{505 \times 4.39 \times 10^{-7}}$$

$$\Delta p^{eq} = 500 \text{ atm} \quad \Delta T^{eq} = +1.58 \text{ K}$$

The melting temperature rises as the pressure rises because all the terms at the right of the equation are positive

In the case of water, the opposite is true since the specific volume of water decreases upon melting



Clapeyron equation in vapor equilibria

Suppose the two phases in equilibrium are a vapor phase and a condensed phase

$$\frac{dp^{eq}}{dT^{eq}} = \frac{\Delta \underline{H}_{vap}}{T^{eq} \underline{V}_{vapor}}$$

Assure the vapor to be an ideal gas

$$\frac{dp^{eq}}{dT^{eq}} = \frac{p^{eq}}{RT^{eq}} \frac{\Delta \underline{H}_{vap}}{T^{eq}}$$

$$d(\ln p^{eq}) = \frac{dp^{eq}}{p^{eq}} = \frac{dT^{eq}}{R} \frac{\Delta \underline{H}_{vap}}{(T^{eq})^2} = -\frac{\Delta \underline{H}_{vap}}{R} d\left(\frac{1}{T^{eq}}\right)$$

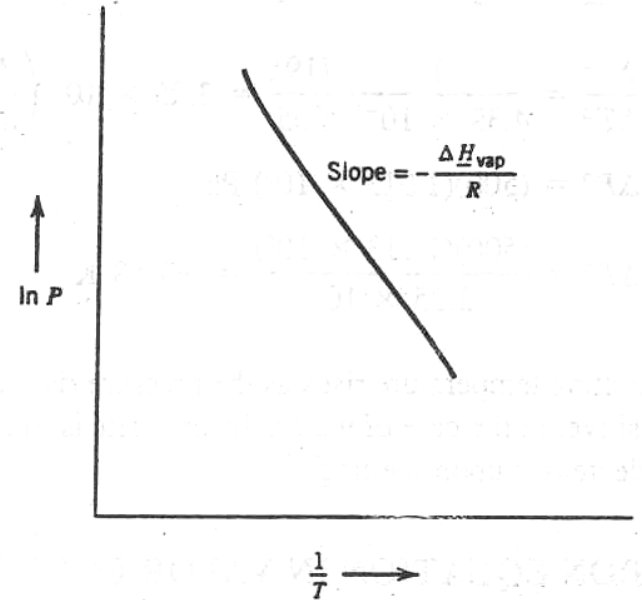


Figure 4.5 Natural logarithms of saturation pressure versus inverse of absolute temperature.

A convenient determination of the enthalpy of evaporation of a condensed phase.



Variation of vapor pressure of a condensed phase with total applied pressure

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Phase Transformation and Applications

Increasing the pressure on the liquid increases the vapor pressure

π_e : equilibrium vapor pressure

π : the vapor pressure of the liquid under a total pressure p_T

The specific Gibbs free energy changes when the liquid is pressurized from π_e to p_T

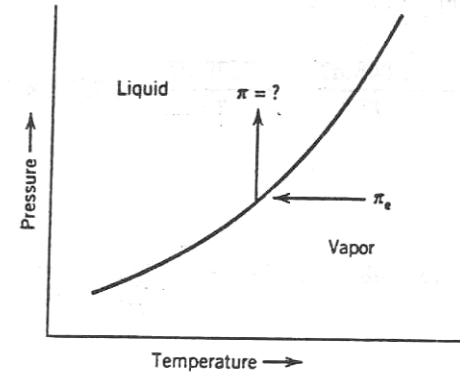


Figure 4.6 Effect of total pressure on vapor pressure.

$$d\underline{G}_l = \underline{V}_l dp$$

$$\Delta\underline{G}_l = \underline{V}_l \Delta p = \underline{V}_l (p_T - \pi_e)$$

The Gibbs free energy of the gas must also change, assuming it is an ideal gas

$$\Delta\underline{G}_v = RT \ln \frac{\pi}{\pi_e} \quad \underline{V}_l (p_T - \pi_e) = RT \ln \frac{\pi}{\pi_e}$$



Variation of vapor pressure of a condensed phase with total applied pressure (2)

$$\underline{V}_l(p_T - \pi_e) = RT \ln \frac{\pi}{\pi_e}$$

If $p_T \gg \pi_e$

$$\underline{V}_l p_T = RT \ln \frac{\pi}{\pi_e}$$

The fractional change of the vapor pressure of water at 298 K when the total pressure of the system is increased to 10 atm

The equilibrium vapor pressure of water is 0.031 atm

$$\ln \frac{\pi}{\pi_e} = \ln \left(1 + \frac{\Delta \pi}{\pi_e} \right) = \frac{\Delta \pi}{\pi_e} = 0.0074$$

1 atm \rightarrow 10 atm

Vapor pressure changes by 0.74 %



Variation of vapor pressure with particle size

The pressure on a small droplet is the sum of the imposed gas pressure and the internal pressure generated by the surface tension of the material

$$2\pi r\gamma = \pi r^2 \Delta p$$

$$\Delta p = \frac{2\gamma}{r}$$

$$\underline{V}_l \left(\frac{2\gamma}{r} \right) = RT \ln \frac{\pi}{\pi_e}$$

$$\ln \frac{\pi}{\pi_e} = \frac{\underline{V}_l}{RT} \left(\frac{2\gamma}{r} \right)$$

$$\underline{V}_l p_T = RT \ln \frac{\pi}{\pi_e}$$

The vapor pressure above the small particles is greater than the vapor pressure above the large particles. Material would then move through the gas phase from small particles to larger ones. Coarsening

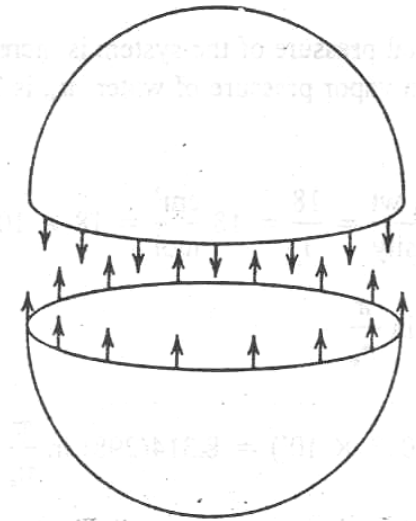


Figure 4.7 The force holding two hemispheres together is $2\pi r\gamma$; the force pushing them apart is $\pi r^2 \Delta P$, where $\Delta P = 2\gamma/r$.



Second-order transition

First derivatives of G with respect to T and p are continuous and the second derivatives of G with respect to T and P are discontinuous

$$\underline{S}_A = \underline{S}_B$$

$$d\underline{S} = \left(\frac{\partial \underline{S}}{\partial T} \right)_p dT + \left(\frac{\partial \underline{S}}{\partial p} \right)_T dp$$

$$d\underline{S} = \frac{C_p}{T} dT - \left(\frac{\partial \underline{V}}{\partial T} \right)_p dp$$

$$\underline{S} = \underline{S}(T, p)$$

$$C_p = T \left(\frac{\partial \underline{S}}{\partial T} \right)_p$$



Second-order transition (2)

$$d\underline{S} = \frac{C_p}{T} dT - \left(\frac{\partial \underline{V}}{\partial T} \right)_p dp$$

$$d\underline{S}_A = d\underline{S}_B$$

$$d\underline{S}_A - d\underline{S}_B = 0 = \frac{C_{p,B} - C_{p,A}}{T^{eq}} dT^{eq} - (\underline{V}_B \alpha_B - \underline{V}_A \alpha_A) dp^{eq}$$

$$\underline{V}_A = \underline{V}_B = \underline{V}$$

$$\frac{dp^{eq}}{dT^{eq}} = \frac{\Delta C_p}{\underline{V} T^{eq} \Delta \alpha}$$

The thermal expansion coefficient does change!

$$\frac{dp^{eq}}{dT^{eq}} = \frac{\Delta \alpha}{\Delta \beta}$$



Superconductivity: an example

$$C_n - C_s = -VT_c \mu_0 \left(\frac{\partial H}{\partial T} \right)_{at T=T_c}^2 \neq 0$$

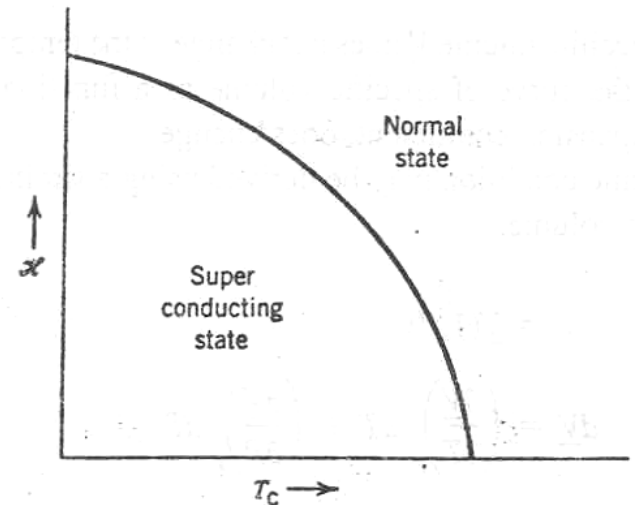


Figure 4.8 Critical temperature as a function of magnetic field for a superconducting material.



Review

Condition of equilibrium

Phase equilibrium

$$\mu_{i,2} = \mu_{i,1}$$

$$\delta W_{rev.1 \rightarrow 2} = 0$$

$$\bar{G}_{i,2} = \bar{G}_{i,1}$$

First order transitions: variation of equilibrium pressure with temperature

Clapeyron equation in vapor equilibria

Variation of vapor pressure of a condensed phase with total applied pressure

Variation of vapor pressure with particle size

Second-order transition

$$\frac{dp^{eq}}{dT^{eq}} = \frac{\Delta C_p}{VT^{eq} \Delta \alpha}$$

$$\frac{dp^{eq}}{dT^{eq}} = \frac{\Delta H}{T^{eq} \Delta V}$$

Clapeyron equation



Homework

Exercises in Chap 4

P116, 4.3, 4.10

在前四章中，写出至少10个需要查词典的词汇
(包括英语单词或词组和中文译名)

请发至：jies@sjtu.edu.cn